Docket No. 245837US2/tca

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Herman Philip GODFRIED, et al.	GAU: 1722
SERIAL NO: 10/717,566	EXAMINER:
FILED: November 21, 2003	
FOR: OPTICAL QUALITY DIAMOND MATERIAL	

REQUEST FOR PRIORITY

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

☐ Full benefit of the filing date of U.S. Application Serial Number , filed , is claimed pursuant to the provisions of **35 U.S.C. §120.**

☐ Full benefit of the filing date(s) of U.S. Provisional Application(s) is claimed pursuant to the provisions of **35 U.S.C. §119(e):**   **Application No.**   **Date Filed**

■ Applicants claim any right to priority from any earlier filed applications to which they may be entitled pursuant to the provisions of **35 U.S.C. §119**, as noted below.

In the matter of the above-identified application for patent, notice is hereby given that the applicants claim as priority:

COUNTRY	APPLICATION NUMBER	MONTH/DAY/YEAR
UNITED KINGDOM	0227261.5	November 21, 2002

Certified copies of the corresponding Convention Application(s)

■ are submitted herewith

☐ will be submitted prior to payment of the Final Fee

☐ were filed in prior application Serial No. filed

☐ were submitted to the International Bureau in PCT Application Number
Receipt of the certified copies by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.

☐ (A) Application Serial No.(s) were filed in prior application Serial No. filed ; and

☐ (B) Application Serial No.(s)

   ☐ are submitted herewith

   ☐ will be submitted prior to payment of the Final Fee

Respectfully Submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.

Joseph Scafetta Jr.

Marvin J. Spivak
Registration No. 24,913

Joseph Scafetta, Jr.
Registration No. 26,803

Customer Number

22850

Tel. (703) 413-3000
Fax. (703) 413-2220
(OSMMN 05/03)

THIS PAGE BLANK (USPTO)

10/717,566

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Dated   15 December 2003

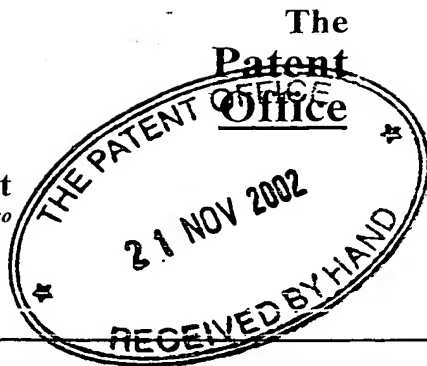**CERTIFIED COPY OF
PRIORITY DOCUMENT**

BEST AVAILABLE COPY

Patents Form 1/77

Patents Act 1977
(Rule 16)

The Patent Office

(stamp) THE PATENT OFFICE · 21 NOV 2002 · RECEIVED BY HAND

22NOV02 E7@489/1 000019
P01/7700 0.00-0227261.5

1/77

Request for grant of a patent
(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1.	Your reference	PA134057/P (P032442GB)

2.	Patent application number *(The Patent Office will fill in this part)*	**0227261.5** 2ı ... 2002

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

**Element Six Limited
Isle of Man Freeport
Ballasalla
Isle of Man
IM99 6AQ**

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

Isle of Man, U.K.

0847995800 *(handwritten)*

4. Title of the invention

Optical Quality Diamond Material

5. Name of your agent *(if you have one)*

Carpmaels & Ransford

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

**43 Bloomsbury Square
London
WC1A 2RA**

Patents ADP number *(if you know it)*

83001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number	Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application		Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
   a) *any applicant named in part 3 is not an inventor, or*
   b) *there is an inventor who is not named as an applicant, or*
   c) *any named applicant is a corporate body*

   Yes

   See note (d))

9. Enter the number of sheets for any of the
   following items you are filing with this form.
   Do not count copies of the same document

   Continuation sheets of this form

   Description   **40**

   Claim(s)

   Abstract

   Drawing(s)   1   + (_(signature)_

10. If you are also filing any of the following,
    state how many against each item.

    Priority documents

    Translations of priority documents

    Statement of inventorship and right
    to grant of a patent *(Patents Form 7/77)*

    Request for preliminary examination
    and search *(Patents Form 9/77)*

    Request for substantive examination
    (Patents Form 10/77)

    Any other documents
    (please specify)

11.   I/We request the grant of a patent on the basis of this application.

    Signature   _Carpmaels & Ransford_   Date   21st November 2002
                   Carpmaels & Ransford

12. Name and daytime telephone number of
    person to contact in the United Kingdom   **Mr. A.J. Jones**   **020-7242 8692**

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) *If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.*
b) *Write your answers in capital letters using black ink or you may type them.*
c) *If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*
d) *If you have answered 'Yes' Patents Form 7/77 will need to be filed.*
e) *Once you have filled in the form you must remember to sign and date it.*
f) *For details of the fee and ways to pay please contact the Patent Office.*

OPTICAL QUALITY DIAMOND MATERIAL

BACKGROUND OF THE INVENTION

This invention relates to chemical vapour deposition (CVD) diamond material, its production and optical devices and elements arising from this material.

There is a range of optical devices which, as a result of their unique requirements, place high demands on the material used for them. Examples include laser windows, where high intensity beams need to pass undisturbed through a window which is required to provide some form of isolation, and other devices such as optical reflectors, diffraction gratings and etalons.

Depending on the particular application, key properties that may play a role in the selection or manufacturing of an appropriate material include low and uniform birefringence, uniform and high refractive index, low induced birefringence or refractive index variation as a function of strain, low and uniform optical absorption, low and uniform optical scatter, high optical (laser) damage threshold, high thermal conductivity (minimising temperature variation), an ability to be processed to show a high surface polish together with high parallelism and flatness, mechanical strength, abrasion resistance, chemical inertness, and repeatability in the material parameters so that it is reliable in the application.

Many materials fulfil one or more of these requirements, but most applications require more than one, and often the material chosen is a compromise, limiting the final performance.

- 2 -

SUMMARY OF THE INVENTION

According to the present invention, a CVD single crystal diamond material shows at least one, preferably at least two, more preferably at least three, and even more preferably at least four of the following characteristics, when measured at room temperature (nominally 20°C):

1) High optical homogeneity, with the transmitted wavefront (as for example measured by a ZYGO GPI phase shifting 633 nm Fizeau-type laser interferometer) differing from the expected geometrical wavefront during transmission through diamond of a thickness of at least 0.5 mm, preferably at least 0.8 mm and more preferably at least 1.2 mm, processed to an appropriate flatness, and measured over lateral dimensions of at least 1.3 mm x 1.3 mm, and preferably at least 2.5 mm x 2.5 mm, and more preferably at least 4.0 mm x 4.0 mm, by less than 2 fringes, and preferably by less than 1 fringe, and more preferably by less than 0.5 fringes, and even more preferably by less than 0.1 fringes, and even more preferably by less than 0.05 fringes, where 1 fringe corresponds' to a difference in optical path length equal to ½ of the measurement wavelength of 633 nm.

2) An effective refractive index in samples at least 0.5 mm thick, preferably at least 0.8 mm and more preferably at least 1.2 mm thick, and measured over lateral dimensions of at least 1.3 mm x 1.3 mm, and preferably at least 2.5 mm x 2.5 mm, and more preferably at least 4 mm x 4 mm, which has a value of 2.3964 to within an accuracy of +/-0.002, and preferably to within an accuracy of +/-0.001, and more preferably to within an accuracy of +/-0.0005, when measured at wavelengths near 1.55 μm by scanning the frequency of the laser beam incident on the sample in the form of an etalon over the frequency range of 197 – 192 THz, recording the transmission of the sample

- 3 -

etalon as a function of frequency, and applying the formula for the Free Spectral Range (equation 1 defined later). Those skilled in the art will understand that the value of 2.3964 is based on the diamond consisting of carbon isotopes in their natural abundance ratio, and that the value of 2.3964 will vary as the isotopic composition of the diamond varies.

3) Low optical birefringence, indicative of low strain such that in samples at least 0.5 mm thick, preferably at least 0.8 mm and more preferably at least 1.2 mm thick, measured over lateral dimensions of at least 1.3 mm x 1.3 mm, and preferably at least 2.5 mm x 2.5 mm, and more preferably at least 4 mm x 4 mm, the modulus of the sine of the phase shift, $|\sin \delta|$, as measured by a Deltascan or similar instrument with similar resolution using radiation in the range 545 – 615 nm and preferably 589.6 nm does not exceed certain limits. Specifically, these limits are that the modulus of the sine of the phase shift, $|\sin \delta|$ for at least 95%, and preferably for at least 98%, and more preferably for at least 99% and even more preferably for 100% of the analysed area of the sample remains in first order (δ does not exceed $\pi/2$) and that $|\sin \delta|$ does not exceed 0.9, and preferably does not exceed 0.6, and more preferably does not exceed 0.4, and more preferably does not exceed 0.3, and more preferably does not exceed 0.2, and more preferably does not exceed 0.1, and more preferably does not exceed 0.05, and more preferably does not exceed 0.03.

4) A combination of optical properties such that a suitably prepared diamond plate in the form of an etalon which is at least 0.5 mm thick, preferably at least 0.8 mm and more preferably at least 1.2 mm thick, with lateral dimensions of at least 1.3 mm x 1.3 mm, and preferably 2.5 mm x 2.5 mm, and more preferably at least 4 mm x 4 mm, and measured using a 1.55 µm wavelength laser beam with a nominal diameter of 1.2 mm, exhibits a free spectral range (FSR) which, when

- 4 -

measured at different positions over the plate varies by less than 5 x 10^{-3} cm^{-1}, and preferably by less than 2 x 10^{-3} cm^{-1}, and more preferably by less than 5 x 10^{-4} cm^{-1}, and even more preferably by less than 2 x 10^{-4} cm^{-1}.

5) A combination of optical properties such that a suitably prepared diamond plate in the form of an etalon which is at least 0.5 mm thick, preferably at least 0.8 mm and more preferably at least 1.2 mm thick, with lateral dimensions of at least 1.3 mm x 1.3 mm and preferably at least 2.5 mm x 2.5 mm, and more preferably at least 4 mm x 4 mm, and measured using a 1.55 μm wavelength laser beam with a nominal diameter of 1.2 mm, and which has no coatings applied to the opticallyprepared surfaces, exhibits when measured at different positions over the plate a contrast ratio exceeding 1.5 and preferably exceeding 1.6 and more preferably exceeding 1.7 and even more preferably exceeding 1.8 and most preferably exceeding 1.9. The contrast ratio is defined as the ratio of the value of the etalon transmission at an incident laser wavelength near 1.55 μm where the transmission has a maximum value to the value of the etalon transmission at an incident laser wavelength near 1.55 μm where the transmission has a minimum value and the transmission value is defined as the ratio of the optical power of a laser beam that is transmitted through the etalon to the laser power that is incident on the etalon.

6) A combination of optical properties such that a suitably prepared diamond plate in the form of an etalon which is at least 0.5 mm thick, preferably at least 0.8 mm and more preferably at least 1.2 mm thick, with lateral dimensions of at least 1.3 mm x 1.3 mm, and preferably at least 2.5 mm x 2.5 mm, and more preferably at least 4 mm x 4 mm, and measured using a 1.55 μm wavelength laser beam with a diameter of

- 5 -

1.2 mm, exhibits an insertion loss not exceeding 3 dB and preferably not exceeding 1 dB and more preferably not exceeding 0.5 dB and even more preferably not exceeding 0.3 dB and most preferably not exceeding 0.1 dB.

7) Low and uniform optical absorption, such that a sample at least 0.5 mm thick, preferably 0.8 mm thick and more preferably at least 1.2 mm thick, has an optical absorption coefficient at a wavelength of 10.6 µm measured near 20°C of less than 0.04 cm^{-1}, and preferably less than 0.03 cm^{-1}, and more preferably less than 0.027 cm^{-1}, and even more preferably less than 0.025 cm^{-1}.

8) A low and uniform optical absorption at a wavelength of 1.06 µm, such that a sample at least 0.5 mm thick, preferably 0.8 mm thick and more preferably at least 1.2 mm thick, has an optical absorption coefficient at 1.06 µm of less than 0.09 cm^{-1}, and preferably less than 0.05 cm^{-1}, and more preferably less than 0.02 cm^{-1}, and even more preferably less than 0.01 cm^{-1}.

9) Low and uniform optical scatter, such that for a sample at least 0.5 mm thick, preferably 0.8 mm thick and more preferably at least 1.2 mm thick, and lateral dimensions of at least 1.3 mm x 1.3 mm, and preferably at least 2.5 mm x 2.5 mm, and more preferably at least 4 mm x 4 mm the forward scatter at a wavelength of 0.63 µm, integrated over a solid angle from 0.3° to 45° from the transmitted beam, is less than 0.2%, and preferably less than 0.1%, and more preferably less than 0.05%, and even more preferably less than 0.03%.

10) Low and uniform optical scatter, such that for a sample at least 0.5 mm thick, preferably at least 0.8 mm thick, and more preferably at least 1.2 mm thick, and with lateral dimensions of at least 1.3 mm x 1.3 mm,

and preferably at least 2.5 mm x 2.5 mm, and more preferably at least 4 mm x 4 mm, the forward scatter at a wavelength of 10.6 μm, integrated over the solid angle from 1.1° to 45° from the transmitted beam, is less than 0.004%, and preferably less than 0.002%, and more preferably less than 0.001%, and even more preferably less than 0.0005%.

11) A high laser damage threshold, such that at a wavelength of 10.6 μm using a Gaussian beam profile with a primary pulse spike of 50 – 100 ns and normalised to a 100 μm 1/e spot size, the mean of the lowest incident peak energy density that causes damage and the highest incident peak energy density that does not cause damage is greater than 120 Jcm^{-2}, and preferably greater than 220 Jcm^{-2}, and more preferably greater than 320 Jcm^{-2}, and even more preferably greater than 420 Jcm^{-2}.

12) A high laser damage threshold, such that at a wavelength of 1.06 μm using a Gaussian beam profile, with a primary pulse spike of 10-50 ps and more preferably 20-40 ps, and normalised to a 100 μm 1/e spot size, the mean of the lowest incident peak energy density that causes damage and the highest incident peak energy density that does not cause damage is greater than 35 Jcm^{-2}, and preferably greater than 50 Jcm^{-2}, and more preferably greater than 80 Jcm^{-2}, and even more preferably greater than 120 Jcm^{-2}, and even more preferably greater than 150 Jcm^{-2}.

13) High thermal conductivity, with a value for material composed of carbon in its natural isotopic abundance which is greater than 1500 $Wm^{-1}K^{-1}$, preferably greater than 1800 $Wm^{-1}K^{-1}$, more preferably greater than 2100 $Wm^{-1}K^{-1}$, even more preferably greater than 2300 $Wm^{-1}K^{-1}$, and even more preferably greater than 2500 $Wm^{-1}K^{-1}$. Those skilled in the art will understand that this is based on the diamond containing

- 7 -

carbon isotopes in their natural abundance ratio, and that the figures will vary as the isotopic composition of the diamond varies.

14) An ability to be processed to show a high surface polish over an area of at least 1.3 mm x 1.3 mm, and preferably at least 2.5 mm x 2.5 mm, and more preferably at least 4.0 mm x 4.0 mm, with an R_a (arithmetic mean of the absolute deviation from the mean line through the profile) less than 2 nm, and preferably less than 1 nm, and more preferably less than 0.6 nm, and even more preferably less than 0.4 nm, and even more preferably 0.2 nm, and even more preferably less than 0.1 nm.

15) An ability to be processed to show a high parallelism, with a parallelism over an area of at least 1.3 mm x 1.3 mm, and preferably at least 2.5 mm x 2.5 mm, and more preferably at least 4.0 mm x 4.0 mm, which is better than 1 arc minute, and preferably better than ±30 arc seconds, and more preferably better than ±15 arc seconds, and even more preferably better than ±5 arc seconds.

16) An ability to be processed to show a high flatness, with a flatness measured using 633 nm radiation over an area of at least 1.3 mm x 1.3 mm, and preferably at least 2.5 mm x 2.5 mm, and more preferably at least 4.0 mm x 4.0 mm, which is better than 10 fringes, and preferably better than 1 fringe, and more preferably better than 0.3 fringes, and even more preferably better than 0.05 fringes.

17) A mechanical design strength, obtained from measurements made using a single cantilever beam technique with individual sample dimensions of 5.0 mm by 3.0 mm by 0.17-0.35 mm (length by breadth by thickness), in which at least 70% and preferably at least 80%, and more preferably at least 90%, and even more preferably at least 95% of samples tested over a batch size of at least 8, and preferably at least

- 8 -

10, and more preferably at least 15, will only fail at strength values in excess of 2.5 GPa, and preferably in excess of 3.0 GPa, and more preferably in excess of 3.5 GPa, and even more preferably in excess of 4.0 GPa.

The diamond material is preferably formed into a mechanical layer or an optical layer or polished gemstone, and more preferably an optical layer, and preferably exceeds one, more preferably two, and even more preferably three, of the following dimensions:

a)   a lateral dimension of 1 mm, preferably 2 mm, more preferably 5 mm and even more preferably 8 mm,

b)   a second orthogonal lateral dimension of 1 mm, preferably 2 mm, more preferably 5 mm and even more preferably 8 mm,

c)   a thickness of 0.1 mm, preferably 0.3 mm, more preferably 0.5 mm, and even more preferably 0.8 mm.

The invention extends to a single crystal CVD diamond material as described above for use in, or as, an optical device or element. Such device or element may be suitable for use in a wide range of optical applications, including, but not limited to, optical windows, laser windows, optical reflectors, optical refractors and gratings, and etalons. For applications requiring reflection at one or more surfaces such as beam splitters or etalons, the diamond may be used uncoated on these surfaces. In addition the material is advantageous as a polished gemstone, in which form it may be initially produced as much thicker layer prior to polishing, typically 2.5 mm and more typically 3.5 mm thick or greater. Properties particularly applicable to this application include the uniformity of optical characteristics, the low scatter and absorption, and the ease of processing and the quality of the processed surface, which, particularly in combination, provides for a more brilliant stone.

- 9 -

The diamond material of the invention can be tailored to specific applications, and although it may not be endowed with all of the above properties in all cases, in many applications it is the ability of the diamond material to show a substantial set or particular combination of the above properties which makes its use particularly beneficial. For example, for use as an etalon, the material may require optical homogeneity, low absorption, high thermal conductivity, and the ability to be processed flat and parallel, but laser damage thresholds and mechanical strength may be less important. Conversely, in application as a viewing or optical access window, the strength may be important, as may be the scatter, the absorption, and characteristics affecting image quality.

An optical device which includes or comprises a CVD diamond material of the invention may have attached to it or built into it either a heat source or a temperature or other measuring device, or both. The heat source provides the ability to alter the temperature of the optical device, and thus any temperature dependent properties, and the temperature sensor a means by which to monitor this and in some instances provide feedback control. This technique is particularly applicable to diamond because its high thermal conductivity ensures the input heat is distributed uniformly very rapidly. Particular embodiments of this form of the invention may be the incorporation of doped layers or tracks using dopants such as boron to form the heater elements, and also further doped structures for the measurement of the temperature. Such doped structures could be produced by ion implantation or by other surface processing techniques.

In application, the material may be further treated, such treatments including mountings, metallisations (such as for gratings), coatings (such as anti-reflection coatings), or the like.

- 10 -

According to another aspect of the invention, a method of producing a CVD diamond material suitable for optical applications comprises growing a single crystal diamond on a substrate by a CVD method in the presence of a controlled low level of nitrogen to control the development of crystal defects.

The level of nitrogen used in the method is selected to be sufficient to prevent or reduce local strain generating defects whilst being low enough to prevent or reduce deleterious absorptions and crystal quality degradation.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described in more detail, by way of example only, with reference to the accompanying drawings in which:

Figure 1   is a schematic side view of a solid etalon showing a typical reflectance and transmittance pattern of a beam incident on a first surface thereof; and

Figure 2   is a graphical representation of a typical transmission characteristic of a solid etalon.

DESCRIPTION OF EMBODIMENTS

The CVD diamond material of the invention is produced by a CVD method in the presence of a controlled low level of nitrogen. The level of nitrogen utilised is critical in controlling the development of crystal defects and thus achieving a diamond material having the key characteristics of the invention. It has been found that material grown with high levels of nitrogen show deleterious absorptions. High levels of nitrogen may also degrade the crystal quality of the material. Conversely, material grown under conditions with essentially no

- 11 -

nitrogen, or less than 300 ppb of nitrogen has a comparatively higher level of local strain generating defects, which affect directly or indirectly many of the high performance optical properties of the diamond. The exact mechanism of this is not well understood, but the following observations have been made. In what follows the word 'dislocations' is intended to cover both isolated dislocations and dislocation bundles where dislocations are grouped together.

No material can be made entirely free of dislocations and other crystal defects over large volumes. The sensitivity of different properties to such crystal defects varies. For example, the average refractive index is relatively insensitive, although local variations of this are quite sensitive. Engineering optical properties, at the high level of precision required, appear to be extremely sensitive to dislocations.

The method of this invention is primarily applicable to growth on a {100} substrate face, and this is assumed unless otherwise stated.

In the absence of sufficient nitrogen in the gas mixture of the growth process, pits form on the {100} growth surface around dislocations which pre-exist in the substrate material or are generated at the substrate/growth interface. Whether because of these pits or otherwise, dislocations can slowly multiply during growth. To a certain extent this process is exponential, with the rate of dislocation multiplication dependent on the existing local dislocation density and arrangement.

In the presence of small amounts of nitrogen, relative facet growth rates are changed and these pits can be removed. Whether because of the absence of these pits or otherwise, dislocation multiplication can be reduced or totally avoided.

These pits may also be responsible for the inclusion of other defects and impurities in the material.

A further effect has been noted, which may form an important part of the process. At typical process conditions without nitrogen the epitaxial growth takes place with the progression of <110> surface steps moving across the substrate surface. These steps are typically just visible under a standard optical microscope, although their presence is generally best confirmed using Nomarski techniques or other high sensitivity techniques. Under the right conditions increasing the nitrogen, within the very low levels of this invention, does not affect the morphology of these surface steps. With these steps present, the uptake of N into the diamond is generally low.

As the nitrogen level increases, the surface growth mechanism undergoes a transition. The surface steps of the diamond become more random and more generally centred around the <100> orientation, at least on a macroscopic scale, and the steps become larger and rougher. These steps are easily seen by microscope, and can often be seen by eye. In the presence of these steps nitrogen incorporation increases substantially and is generally non-uniform on a microscopic scale. The concentration of nitrogen at which this transition occurs is a sensitive function of the growth conditions, including temperature and pressure, but is typically around 1.8 ppm (of total gas concentration, when using N_2) for the processes described herein. For small excursions above this limit, some of the benefits of the method of the invention may still be realised, particularly for example the mechanical strength or the surface processing, but properties such as optical absorption are adversely affected by significant nitrogen incorporation, which easily occurs once <100> steps are present.

- 13 -

The lower bound to the concentration of N in the process gas is thus set by the need to limit pitting and control the strain generating defects, and the upper bound to the concentration of nitrogen in the process gas set by the onset of deleterious absorptions and other types of defect generation, and the role that the change in surface step growth mechanism has on these. However, these bounds are process dependent, such that they may vary according to the process conditions used, including the actual gaseous source of N, and also the specific material properties required, and are best illustrated by way of example. Typically however in the method of the invention, the upper bound on the nitrogen level in the gas phase (ppm N_2, or the equivalent of the actual nitrogen source used to provide the same total N) is 5 ppm, and preferably 2 ppm, and more preferably 1.5 ppm, and even more preferably 1ppm. The lower bound on the nitrogen level in the gas phase (ppm N_2, or the equivalent of the actual nitrogen source used to provide the same total nitrogen) is greater than 300 ppb, and preferably greater than 500 ppb, and more preferably greater than 700 ppb, and even more preferably greater than 800 ppb.

Using the above conditions it has been possible to produce the single crystal CVD diamond material of the invention, typically in layer form, with advantageous optical properties.

It is important for the production of a diamond optical layer of the invention that growth of a layer of single crystal CVD diamond takes place on a diamond surface which is substantially free of crystal defects. In this context, defects primarily mean dislocations and micro cracks, but also include twin boundaries, point defects not intrinsically associated with the dopant N atoms, low angle boundaries and any other extended disruption to the crystal lattice. Preferably the substrate is a low birefringence type Ia natural, Ib or IIa high pressure/high temperature synthetic diamond or a CVD synthesised single crystal diamond.

- 14 -

The quality of growth on a substrate which is not substantially free of defects rapidly degrades as the layer grows thicker and the defect structures multiply, causing general crystal degradation, twinning and renucleation. Defects of this type are particularly deleterious to the present application, causing local variations in many of the key properties.

The defect density is most easily characterised by optical evaluation after using a plasma or chemical etch optimised to reveal the defects (referred to as a revealing plasma etch), using for example a brief plasma etch of the type described below. Two types of defects can be revealed:

1)   Those intrinsic to the substrate material quality. In selected natural diamond the density of these defects can be as low as $50/mm^2$ with more typical values being $10^2/mm^2$, whilst in others it can be $10^6/mm^2$ or greater.

2)   Those resulting from polishing, including dislocation structures and microcracks forming chatter tracks along polishing lines. The density of these can vary considerably over a sample, with typical values ranging from about $10^2/mm^2$, up to more than $10^4/mm^2$ in poorly polished regions or samples.

The preferred low density of defects is such that the density of surface etch features related to defects, as described above, are below $5 \times 10^3/mm^2$, and more preferably below $10^2/mm^2$.

The defect level at and below the substrate surface on which the CVD growth takes place may thus be minimised by careful preparation of the substrate. Included here under preparation is any process applied to the material from mine recovery (in the case of natural diamond) or synthesis (in the case of synthetic material) as each stage can influence the defect density within the material at

the plane which will ultimately form the substrate surface when preparation as a substrate is complete. Particular processing steps may include conventional diamond processes such as mechanical sawing, lapping and polishing (in this application specifically optimised for low defect levels), and less conventional techniques such as laser processing or ion implantation and lift-off techniques, chemical/mechanical polishing, and both liquid chemical processing and plasma processing techniques. In addition, the surface R_Q measured by stylus profilometer, preferably measured over 0,08 mm length) should be minimised, typical values prior to any plasma etch being no more than a few nanometers, i.e. less than 10 nanometers. R_Q is the root mean square deviation of surface profile from flat (for a Gaussian distribution of surface heights, R_Q=1.25 R_a: for definitions, see for example "Tribology: Friction and Wear of Engineering Materials", IM Hutchings, (1992), Publ. Edward Arnold, ISBN 0-340-56184)

One specific method of minimising the surface damage of the substrate is to include an *in situ* plasma etch on the surface on which the homoepitaxial diamond growth is to occur. In principle this etch need not be *in situ*, nor immediately prior to the growth process, but the greatest benefit is achieved if it is *in situ*, because it avoids any risk of further physical damage or chemical contamination. An *in situ* etch is also generally most convenient when the growth process is also plasma based. The plasma etch can use similar conditions to the deposition or diamond growing process, but with the absence of any carbon containing source gas and generally at a slightly lower temperature to give better control of the etch rate. For example, it can consist of one or more of:

(i)   an oxygen etch using predominantly hydrogen with optionally a small amount of Ar and a required small amount of O_2. Typical oxygen etch conditions are pressures of 50-450 x 10^2 Pa, an etching gas containing an oxygen content of 1 to 4 percent, an argon content of 0 to 30 percent and the balance hydrogen, all

- 16 -

percentages being by volume, with a substrate temperature 600-1100°C (more typically 800°C) and a typical duration of 3-60 minutes.

(ii)   a hydrogen etch which is similar to (i) but where the oxygen is absent.

(iii)   alternative methods for the etch not solely based on argon, hydrogen and oxygen may be used, for example, those utilising halogens, other inert gases or nitrogen.

Typically the etch consists of an oxygen etch followed by a hydrogen etch and then moving directly into synthesis by the introduction of the carbon source gas. The etch time/temperature is selected to enable remaining surface damage from processing to be removed, and for any surface contaminants to be removed, but without forming a highly roughened surface and without etching extensively along extended defects such as dislocations which intersect the surface and thus cause deep pits. As the etch is aggressive, it is particularly important for this stage that the chamber design and material selection for its components be such that no material is transferred by the plasma from the chamber into the gas phase or to the substrate surface. The hydrogen etch following the oxygen etch is less specific to crystal defects rounding off the angularities caused by the oxygen etch which aggressively attacks such defects and providing a smoother, better surface for subsequent growth.

The primary surface of the diamond substrate on which the CVD diamond growth occurs is preferably the {100} surface. Due to processing constraints, the actual sample surface orientation can differ from this ideal orientation up to 5°, and in some cases up to 10°, although this is less desirable as it adversely affects reproducibility.

It is also important in the method of the invention that the impurity content of the environment in which the CVD growth takes place is properly controlled. More particularly, the diamond growth must take place in the presence of an atmosphere containing substantially no contaminants other than the intentionally added nitrogen. This addition of nitrogen should be accurately controlled, with an error of less than 300 parts per billion (as a molecular fraction of the total gas volume) or 10% of the target value in the gas phase, whichever is the larger, and preferably with an error of less than 200 parts per billion (as a molecular fraction of the total gas volume) or 6% of the target value in the gas phase, whichever is the larger, and more preferably with an error of less than 100 parts per billion (as a molecular fraction of the total gas volume) or 3% of the target value in the gas phase, and even more preferably with an error of less than 50 parts per billion (as a molecular fraction of the total gas volume) or 2% of the target value in the gas phase, whichever is the larger. Measurement of absolute and relative nitrogen concentration in the gas phase at concentrations in the range 300 ppb – 5 ppm requires sophisticated monitoring equipment such as that which can be achieved, for example, by gas chromatography described in WO 01/96634.

The source gas may be any known in the art and will contain a carbon-containing material which dissociates producing radicals or other reactive species. The gas mixture will also generally contain gases suitable to provide hydrogen or a halogen in atomic form, and a source of nitrogen which may be for example N_2 or NH_3.

The dissociation of the source gas is preferably carried out using microwave energy in a reactor, examples of which are known in the art. However, the transfer of any impurities from the reactor should be minimised. A microwave system may be used to ensure that the plasma is placed away from all surfaces except the substrate surface on which diamond growth is to occur and its mount. Examples of preferred mount materials include molybdenum, tungsten, silicon

and silicon carbide. Examples of preferred reactor chamber materials include stainless steel, aluminium, copper, gold and platinum.

A high plasma power density should be used, resulting from high microwave power (typically 3-60kW, for substrate diameters of 25-300 mm) and high gas pressures (50-500 x 10^2Pa, and preferably 100-450 x 10^2Pa).

Applications arising from the CVD diamond material of the invention, where performance is enabled by these unique material properties, include but are not limited to:

- optical windows – for example where very high image quality is required. The consistently high mechanical strength of the material assists in designing for applications where the window is pressurised.

- laser windows - where high intensity beams need to pass undisturbed through a window providing a degree of isolation. It is particularly important that the laser beam does not interact with the window in a manner which degrades the beam, for example by local absorption and thermally induced strains.

- optical reflectors – where a surface needs to be extremely flat or have a very accurately prescribed surface shape and be stable.

- optical refractors and lenses – where one or both surfaces of an optical transmission component are at least in part deliberately non planar or non parallel.

- diffractive optical elements – e.g. where a structure in or on the diamond is used to modify a light beam by diffraction.

- etalons.

For convenience, and by way of an example, the application of the diamond material of the invention to etalons will be described in detail, but those skilled in the art will recognise the general importance of the optical properties of the

- 19 -

CVD diamond material of this invention to other applications such as those indicated above.

An optical system with two partially reflecting surfaces that has been fabricated in such a way as to have a high degree of flatness and parallelism between the two reflecting surfaces is called a *Fabry-Perot Etalon*. Typically the etalon can be made by aligning two very flat partially reflective mirrors such that their reflecting surfaces are parallel and separated by, for instance, an air or controlled gaseous medium gap or a vacuum separation. Alternatively the etalon can be made by polishing two very parallel surfaces 10,12 onto a plate 14 of an optically transparent solid material, called a solid etalon, as depicted schematically in Figure 1 of the accompanying drawings.

A beam incident on the first surface of the etalon is partially transmitted and reflected according to the reflectivity of the surface. The transmitted beam traverses the etalon and subsequently at the second surface is partially transmitted and partially reflected back to the first surface where again partial transmission and reflection take place. As a result interference takes place between transmitted and reflected parallel beams emerging from the etalon. A typical transmission characteristic from an etalon is shown graphically in Figure 2.

The thickness of the etalon controls the separation of subsequent maxima/minima of the etalon characteristic, known as the *free spectral range* FSR, which for normally incident light is given below in terms of frequency,

$$FSR = \frac{c}{2nd} \tag{1}$$

where c is the speed of light in vacuum, d is the thickness of the etalon, and n is the refractive index of the etalon material.

The shape of the transmission curve (e.g. the sharpness of the peaks and/or the depth of the minima) is further influenced by the reflectivity of the etalon surfaces. Different values of the reflectivity may be obtained by applying partially reflecting optical coatings to the etalon surfaces, as is well known in the art. Alternatively one can choose not to apply optical coatings to the etalon surfaces and use the Fresnel reflectivity of the uncoated surfaces of the etalon.

When the etalon transmission curve shows sharp peaks this may be characterised by the *finesse*, F, defined as the ratio of the (frequency) spacing between successive peaks over the full-width-half-maximum of the peaks. For high values of the reflectivity and when losses due to absorption or scatter in the etalon or at the reflecting surfaces and deviations from flatness and parallelism of the reflecting surfaces are so small they can be neglected, the finesse is given by:

$$F = \frac{\pi\sqrt{R}}{(1-R)} \qquad (2)$$

where R is the reflectivity of the etalon surface.

Alternatively, when transmission peaks are not very sharp, one can characterise the etalon transmission curve by specifying the contrast ratio, C. This is given by the ratio of the maximum and minimum transmission values,

$$C = \frac{T_p}{T_v} \qquad (3)$$

where T_p (T_v) is the transmission of the etalon at a frequency equal to one of the peaks (valleys) in the transmission curve.

For etalons where deviations from flatness or parallelism, refractive index variations and absorption or scatter losses can be neglected, C is given by

- 21 -

$$C = 1 + \frac{4R}{(1-R)^2} = \left(\frac{1+\bar{R}}{1-R}\right)^2 \qquad (4)$$

Another useful parameter to characterise the etalon performance is the insertion loss, L, expressed in decibel (dB), which is determined by the transmission of the etalon at the peaks,

$$L = -10 \times^{10} \log(T_p) = -10 \times^{10} \log\left(\frac{I_p}{I_0}\right) \qquad (5)$$

where I_p and I_0 are the transmitted and incident intensities at a frequency equal to one of the peaks in the transmission curve. Thus defined the insertion loss can vary between 0 (no loss) and infinite (no transmission at all). For an ideal etalon without losses and with infinitely flat and parallel surfaces, the insertion loss would be 0.

When deviations from flatness or parallelism, refractive index variations or losses cannot be neglected, the approximate equations (2) and (4) are no longer valid and insertion loss (5) will tend to increase while the contrast ratio generally will be lower.

The important material properties influencing etalon performance, expressed by the parameters free spectral range, insertion loss, contrast ratio and/or finesse, are thus:

R – surface reflectance (either intrinsic when uncoated or of the coating);
α – absorption losses in the bulk of the etalon material or at the surface;
α_{sc} – scatter losses in the bulk of the etalon material or at the surface;
n – refractive index of the etalon material and variations in it (including birefringence, i.e. dependence of the refractive index on polarisation and propagation direction in the material); and
d – flatness and parallelism of the reflecting surfaces.

Diamond has a number of advantages when used as an etalon compared with other materials, including:

a) a high refractive index, which translates into a more compact/thinner etalon;

b) a Fresnel reflectivity which in some applications is high enough so as to make optical coatings unnecessary;

c) a low temperature coefficient of refractive index and a low thermal expansion coefficient, which mean that diamond etalons are less sensitive than other optical materials to temperature changes;

d) a high thermal conductivity, which means that there is minimal variation in the transmission curve caused by temperature variations in the environment or absorption by the light beam (further increases in thermal conductivity are, however, beneficial for this reason);

e) the high strength and stiffness, relative to other materials, and high hardness of diamond, which makes it strong and impervious to scratching (if uncoated) - it also minimises the effects of any mounting induced stresses.

However, the use of diamond as an etalon material has been very limited. The limitation has been the availability of material with suitable properties, particularly those that are sensitive to quality, and in suitable sizes. For example, the most abundant natural diamond is type Ia. Type Ia natural diamonds are generally limited in size, and their price determined by their use as gemstones. Material available for commercial applications is mostly faint yellow coloured (absorbing), contains inclusions (stressed, scattering), and also contains hydrogen, which may give rise to further absorptions in the visible and infrared ranges of the spectrum. The refractive index variations between natural stones can be as high as 1%. Functionality in the intended application can only be assured by costly screening of each piece of material,

- 23 -

which typically can only be performed after substantial processing has taken place.

The CVD diamond material of the invention provides a material, superior to other diamond and other materials, as an etalon material.

The CVD single crystal diamond material of the invention, as described, has one or more key characteristics. Some of these characteristics and the techniques which may be used to measure or determine them will now be described.

OPTICAL CHARACTERISTICS AND MEASUREMENT TECHNIQUES

Optical Homogeneity

The optical homogeneity was measured using a ZYGO GPI phase shifting 633 nm laser Fizeau-type interferometer. Samples were prepared as optical plates 0.8 and 1.25 mm thick and up to 5 mm x 5 mm lateral dimensions with flat polished surfaces. Measurements were made using a 4% reflectivity flat, beam splitter and combining the reflected beam from this beam splitter with the transmitted beam after dual passage through the diamond plate with an intermediate reflection off a 10% reflective flat mirror. Both the beam splitter and the reflective mirror were of interferometric quality with flatness better than approximately 30 nm over their diameters of 100 mm. The resulting interference pattern was recorded with a charge coupled device (CCD) camera and digitally stored. The interference fringes were then analysed using the Transmitted Wavefront Measurement Application module which is supplied as standard software with the Zygo GPI interferometer. Deviations from a perfectly flat wavefront were thus recorded. These deviations are a combination of the effects of non-flatness of the surfaces and optical non-

- 24 -

homogeneity of the diamond material. By polishing the surfaces to high enough flatness (better than 30 nm) the effects of the non-homogeneity could be determined to better than 0.05 fringe, proportionately lower levels of flatness being permissible for less accurate measurements.

Effective Refractive Index

The effective refractive index was measured by first measuring the thickness of an optical plate processed in the shape of an etalon with a digital micrometer with resolution better than 0.5 μm and then measuring the Free Spectral Range of the etalon over the frequency range of 197 THz – 192 THz using light that is perpendicularly incident on the etalon, such that the required accuracy in the effective refractive index could be obtained. The effective refractive index was then found from equation (1) defined earlier. The effective refractive index found by this method can differ slightly from the refractive index found for example by simple application of Snell's law (refraction of light at the interface between two optical media), the value obtained here generally being higher. The difference arises because of the inevitable dispersion present in the diamond, and the fact that the method used here for the effective refractive index is a form of average obtained from the range of frequencies used in the measurement.

Free Spectral Range (FSR)

FSR was measured for a plate suitably processed in the form of an etalon (e.g. 1.5 mm x1.5 mm in the lateral dimensions and 1.25 mm thick, with Transmitted Wavefront accuracy better than 0.05 fringe at 1.55 μm and parallelism of the polished surfaces better than 10 arcsec and surface roughness R_a better than 1 nm). These plates were mounted on a optical stage with translational and rotational capability along two mutually perpendicular axes in the plane of the

diamond etalon. The etalon was then positioned perpendicular to and centered with respect to a collimated beam from a laser diode whose wavelength can be continuously varied between 1.52 and 1.62 µm. The power transmitted through the etalon as a function of the frequency of the light was recorded and stored in digital form in a computer. From the frequency difference between successive peaks in the transmission spectrum the Free Spectral Range was directly determined.

Birefringence

For an isotropic medium, such as stress-free diamond, the refractive index is independent of the direction of the polarization of light. If a diamond is inhomogeneously stressed, either because of grown-in stress or local defects or because of externally applied pressure, the refractive index is anisotropic. The variation of the refractive index with direction of polarization may be represented by a surface called the optical indicatrix that has the general form of an ellipsoid. The difference between any two ellipsoid axes is the linear birefringence for light directed along the third. This may be expressed as a function involving the refractive index of the unstressed material, the stress and opto-elastic coefficients.

The Deltascan (Oxford Cryosystems) gives information on how the refractive index at a given wavelength depends on polarization direction in the plane perpendicular to the viewing direction. An explanation of how the Deltascan works is given by A. M. Glazer et al. in Proc. R. Soc. Lond. A (1996) 452, 2751-2765.

From a series of images captured for a range of different relative orientations of a pair of plane polarising filters the Deltascan determines the direction of the "slow axis", the polarization direction in the plane perpendicular to the viewing

- 26 -

direction for which the refractive index is a maximum. It also measures $|\sin \delta|$ where δ is the phase shift given by

$$\delta = (2\pi / \lambda) \Delta n \, L$$

where λ is the wavelength of the light, L is the thickness of the specimen and Δn is the difference between the refractive index for light polarized parallel to the slow and fast axes. Δn L is known as the 'optical retardation'.

For retardation in first order, with L = 0.6 mm and λ = 589.6 nm, then:
when $\sin \delta = 1$ and $\Delta n \, L = \lambda / 4$, it can be deduced that $\Delta n = 2.45 \times 10^{-4}$.
when $\sin \delta = 0.5$ and $\Delta n \, L = \lambda / 12$, it can be deduced that $\Delta n = 0.819 \times 10^{-4}$.

The Deltascan produces three colour-coded images showing the spatial variations of a) the "slow axis", b) $\sin \delta$ and c) the absorbance at the wavelength of operation.

Samples are prepared as optical plates of known thickness and analysed over an area of at least 1.3 mm x 1.3 mm, and preferably 2.5 mm x 2.5 mm, and more preferably 4 mm x 4 mm. Sets of Deltascan images or 'frames', each covering an area of 1 mm x 0.75 mm, are recorded for each sample at a wavelength of 589.6 nm. Within each frame, the Deltascan individually analyses 640 x 480 pixels, ensuring the sample is analysed at very fine scale. The array of Deltascan $|\sin \delta|$ images is then analysed for the behaviour of sine δ. The simplest analysis is to identify the maximum value of sine δ in each 1 mm x 0.75 mm frame over the whole of the analysis area and use these values to characterise the maximum value of the whole of the area analysed. Where the array of 1 mm x 0.75 mm frames does not exactly match the area under analysis, the frames are arranged to obtain the minimum total number of frames to entirely cover the area, and centred so as to make utilisation of edge

frames as symmetric as practical. That part of the data in any frame which is from outside the boundary of the area under analysis is then excluded from the analysis of that frame. Alternatively, each 1 mm x 0.75 mm frame can be analysed for the maximum value remaining after exclusion of 5%, 2%, or 1% of the data within it that lies within the analysed sample area, so as to obtain the maximum value over 95%, 98%, or 99% respectively of the material of the area analysed.

Optical Absorption

Optical absorption is measured by laser calorimetry, with a thermocouple attached to the sample under test to measure the rise in sample temperature resulting from the passage through the sample of the laser beam of the required wavelength. Such techniques are well known in the art.

Optical Scatter

Methods for the measurement of optical scatter are well known (see for example DC Harris, "Infrared Window and Dome Materials", SPIE, Washington, USA 1992)

Laser damage threshold

The laser damage threshold is measured by firing pulses of a laser at the sample under test, and characterising the point of failure as the mean of the lowest incident peak energy that causes damage and the highest incident peak energy that does not cause damage.

At a wavelength of 10.6 µm, the method used is as follows: a Q-switched CO_2 laser with a primary spike of the order of 50 -100 ns containing typically 1/3 of the total pulse energy, and a much lower peak power relaxation pulse of the

order of 2 µs, and normalised to a 100 µm 1/e spot size). The relaxation pulse can be neglected because this test operates in the time domain where electron avalanche ionisation is the conventional model for damage to occur, which is thus dependent on peak power density (i.e. peak electric field).

At a wavelength of 1.06 µm the method used is as follows: a NdYAG laser with a single spike of 10 - 50 ps duration, and more preferably in the range 20-40 ps, and normalised to a 100 µm 1/e spot size.

Thermal conductivity

Thermal conductivity is measured by the laser flash technique (see for example DJ Twitchen et al., Diamond and Related Materials, 10 (2001) p731, and CJH Wort et al, Diamond and Related Materials, 3 (1994) p1158).

Surface R_a

Surface roughness was measured using a Zygo NewView 5000 scanning white light interferometer. The interferometer utilises a microscope equipped with an interferometric objective of the Michelson or the Mireau type. Magnifications of between 1x to 50x are possible with this system. By measuring over the full area of the diamond plate we found that surface roughness varied by less than 10% over the area of the plate if it was fully fine-polished. Therefore in the current measurements the roughness was inferred from measurement over a representative area of approx. 1 mm x 1 mm.

Surface parallelism

Surface parallelism was measured using a Zygo GPI phase shifting 633 nm laser Fizeau-type interferometer in a set-up identical to the measurement of the transmitted wavefront. By comparing the transmitted wavefront fringe pattern

with the diamond etalon in the beam path with the pattern measured without an etalon in the beam path, the change in direction of and distance between successive fringes was computed and from this the deviation from parallelism between the two polished surfaces of the etalon was determined. These two fringe patterns were measured simultaneously by passing part of the light through the etalon while at some other position the light was directly incident on the 10% reflective flat mirror and was again reflected back towards the detector without passing through the diamond etalon. The simultaneous measurement allowed for higher accuracy than if the two measurements were performed one after the other.

Surface flatness

Surface flatness was measured using a Zygo GPI phase shifting 633 nm laser Fizeau-type interferometer. With this interferometer the light from a 633 nm laser source was partially reflected from a 10% reflectivity, interferometric quality beam splitter and the light transmitted by the beam splitter was partially reflected by the polished surface of a diamond optical component manufactured from the material of the invention. The two reflected beams were combined and the resulting fringe pattern was recorded with a CCD camera detector and stored digitally in a computer. The pattern was subsequently analysed with the flatness application which is included as a standard application in the software of the Zygo GPI interferometer.

Mechanical Strength

The utility of the material of this invention is clearly illustrated by the absence of reported strength data in single crystal diamond which has been obtained by actual fracture tests. Data currently reported is based on indentation tests, and the approximations and assumptions which are inherent in this approach.

Conversely, the method of this invention makes material available in sufficient quantity that proper fracture tests can be completed.

Furthermore, fracture strength testing is a destructive test. Since each piece of natural diamond is unique, once its strength is known then it is no longer available for application. Fracture testing can then only be used to characterise the spread of strength against some proxy characteristic, and the lowest anticipated strength used for application. In contrast, the synthetic diamond of the invention is a well characterised and consistent material such that the fracture strength of a particular element can be reasonably predicted based on fracture statistics of equivalent samples. The design strength of diamond, as used in this specification, is the strength which is exhibited by at least 70%, preferably 80%, more preferably at least 90%, and even more preferably at least 95% of equivalent samples of material tested using the procedure below.

The strength was measured using a single cantilever beam technique, with a sample size of 5.0 mm by 3.0 mm by 0.18-0.35 mm (length, l, by breadth, b, by thickness, d). The samples were cut from {100} oriented plates, with the long axis along the <110> direction (so that the thickness is along the <100> and the length and breadth are along the <110>). The testing procedure mounted the beams with an exposed length of 4 mm (i.e. 1 mm inside the clamp) and applied the force at a distance of 3.5 mm from the clamp.
The strength, σ_b, is given by the expression:

$$\sigma_b = (6Ws)/(bd^2)$$

where W is the breaking load and s is the distance between the loading line and the clamping line.

- 31 -

Test samples were cut from homoepitaxial CVD diamond plates and carefully prepared by scaife polishing on progressively finer and finer grits down to a grit size of approximately 0.1 μm. Poor surface finish can limit the measured strength of the material and the ability of this material to take a high surface finish may contribute to its overall strength.

The invention will now be discussed in further detail by way of the following non-limiting examples.

Example 1

Substrates suitable for synthesising single crystal CVD diamond of the invention may be prepared as follows:

i)   Selection of stock material (type Ia natural stones and type Ib HPHT stones) was optimised on the basis of microscopic investigation and birefringence imaging to identify substrates which were free of strain and imperfections.

ii)   Laser sawing, lapping and polishing to minimise subsurface defects using a method of a revealing plasma etch to determine the defect levels being introduced by the processing.

iii)   After optimisation it was possible routinely to produce substrates in which the density of defects measurable after a revealing etch is dependent primarily on the material quality and is below $5 \times 10^3/mm^2$, and generally below $10^2/mm^2$. Substrates prepared by this process are then used for the subsequent synthesis.

A high temperature/high pressure synthetic type 1b diamond was grown in a high pressure press, and as a substrate using the method described above to

minimise substrate defects to form a polished plate 5 mm x 5 mm square by 500 μm thick, with all faces {100}. The surface roughness R_Q at this stage was less than 1 nm. The substrate was mounted on a tungsten substrate using a high temperature diamond braze. This was introduced into a reactor and an etch and growth cycle commenced as described above, and more particularly:

1) The 2.45 GHz reactor was pre-fitted with point of use purifiers, reducing unintentional contaminant species in the incoming gas stream to below 80 ppb.

2) An *in situ* oxygen plasma etch was performed using 15/75/600 sccm (standard cubic centimetre per second) of $O_2/Ar/H_2$ at 263 x 10^2 Pa and a substrate temperature of 730°C.

3) This moved without interruption into a hydrogen etch with the removal of the O_2 from the gas flow.

4) This moved into the growth process by the addition of the carbon source (in this case CH_4) and dopant gases. In this instance was CH_4 flowing at 36 sccm and 1 ppm N_2 was present in the process gas, provided from a calibrated source of 100 ppm N_2 in H_2 to simplify control. The substrate temperature at this stage was 800°C

5) On completion of the growth period, the substrate was removed from the reactor and the CVD diamond layer removed from the substrate.

The CVD diamond layer grown above can be sufficiently large to produce at least one and preferably several diamond etalons (in a two dimensional array)

- 33 -

depending on the size of the CVD diamond layer and the required size of the etalons.

The diamond layer grown as described above was polished to just above the desired thickness of 1.25 mm, which is the thickness of the desired diamond etalon as defined by the required free spectral range and intended wavelenth of operation, using polishing techniques known in the art.

The plate was then fine polished one side on a cast iron diamond polishing wheel that had been carefully prepared. The tang used was very rigid and held the diamond against a reference surface that ran parallel to the scaife surface.

The diamond plate was then turned over and the other side was polished to the desired flatness and parallelism on the same scaife, taking care at this stage to bring the thickness to that required for the final etalon. Parallelism was measured using a commercial Zygo GPI interferometric instrument based on the Fizeau principle, well known to those skilled in the art. The thickness was measured initially by a micrometer. using measurement of the free spectral range (FSR) as a final stage check. Final thickness was achieved by measuring the linear removal rate, which because of the quality of the material was very constant, and then polishing for the necessary predicted time. Other methods of etching or material removal have been used, including ion beam etching, plasma etching or reactive ion etching.

The plate was then cut up by a laser into discrete units. The side faces were then polished, although this is not always required by the application.

The resultant diamond etalon was 1.5mm square, 1.251 mm thick, made to the following tolerances:

thickness:- ± 0.25 μm

- 34 -

parallelism-: ± 5 arcsec

surface R_a:- 0.5 nm

and had a FSR of $1.6678 \pm 2 \times 10^{-4} \text{cm}^{-1}$.

Another diamond plate from the above synthesis process was used to further characterise the achievable surface R_a. The surface was carefully polished on both sides as described above and then measured for surface R_a using the Zygo NewView 5000 scanning white light interferometer. Measurements were taken each side of the sample, each measurement on a 1 mm x 1 mm area with the 9 areas forming a 3 mm x 3 mm grid on the centre of each side, and then the statistical mean of the 9 measurements was calculated. The measured R_a on side A was 0.53 nm ± 0.04 nm, and on side B was 0.54 nm ± 0.05 nm.

Example 2

A set of 6 mm x 6 mm x 0.4 mm plates of homoepitaxial CVD diamond were synthesised according to the method described in Example 1. From these plates, a set of rectangular test samples, 3 mm x 5 mm in lateral dimensions and 0.17 to 0.22 mm thick were cut, ensuring that the cut pieces were free from growth sector boundaries.

The set of samples was polished on a scaife using a range of diamond powders down to 0.1 μm. Care was taken to ensure that, as far as possible, all sub-surface damage was removed from the samples. The final polishing stage with the finest grit is vital as this controls the final surface flaw size distribution. After the top and bottom surfaces were polished, the edges of the samples were prepared to the same standard. After polishing was complete, the surfaces were examined by Nomarski interference contrast and 'micromapped' to check the surface roughness. Nomarski microscopy at a magnification of

x200 revealed that there where no visible defects in the surface. The surface roughness, as defined by the R_a value, was determined using a non-contact, optical surface roughness measurement instrument ('Micromap'). Two series of 200 µm long scans were made in perpendicular directions and the resulting R_a values were averaged yielding a mean R_a value of less than 0.25 nm. This compares with typical R_a values of between 1 nm and 5 nm for diamonds polished using the same technique as is used for polishing natural diamonds in the jewellery trade.

An additional stage of ion beam etching was applied to the surface of some of the samples prior to final polishing. A further optional technique would be to chemically thin the samples prior to final polishing.

The strength of the plates was measured by single cantilever beam bending. The individual strength values for a set of nine samples approximately 0.2 mm thick were, in GPa, 1.50, 1.63, 2.50, 3.26, 3.30, 4.15, 4.29, 4.83, 5.12. Analysis of this and other datasets suggests that the two lowest values are from a different population to the other seven, possibly indicating that the sample preparation was not sufficiently careful in this instance to avoid any influence on the measured strength. Even with these two suspect datapoints included, 77% of samples have a breaking strength of at least 2.5 GPa, and the data suggests the strength is actually in excess of 3 GPa.

For comparison, there being no equivalent data in the public domain (all known strength measurements on natural diamond are based on indentation testing, which is an indirect and less reliable method, because of the restricted availability of suitable samples), the strength of a batch of five type IIa natural diamond plates was also measured. These plates were carefully selected by examination with an optical microscope at x50 magnification to be free of inclusions and other flaws which may weaken the diamond, and were prepared and tested by the same technique. The individual strength values for this set

- 36 -

of 5 samples approximately 0.18 mm thick were, in GPa, 1.98, 2.08, 2.23, 2.61, 2.94 clearly limited by the intrinsic properties of the material. Similarly type Ib single crystal diamond synthesised by a high pressure-high temperature process were carefully selected, processed, and tested using the same techniques. The individual strength values for this set of 14 samples approximately 0.35 mm thick were, in GPa, 0.94, 1.11, 1.16, 1.3, 1.35, 1.38, 1.46, 1.50, 1.54, 1.6, 1.65, 1.72, 1.73, 1.98, 2.17.

The strength population of the CVD diamond of this invention is clearly distinct and higher than that of either the natural or HPHT diamond .

A particular application of high strength diamond is in optical windows for gas analysis by infrared spectroscopy. A particular window, which is 7 mm in diameter, has a clear aperture of 5 mm and is brazed around the outer 1 mm of one flat surface, has to withstand a pressure differential of 200 atmosphere with a safety factor of 4.

The breaking strength is related to the thickness, t, by:

$$t = \sqrt{(3r^2 Pk/8\sigma_b)}$$

where r is the clear aperture, P, the pressure, σ_b, the breaking strength and k a constraint factor which, for diamond, is 3.1 for unconstrained at the edge and 1.1 for fully constrained at the edge (assuming Poissons ratio for diamond to have a value of 0.1). Because determining the degree of constraint is difficult, we take the worst-case scenario of the edge being unconstrained.

If a natural diamond window (design strength 2.0 MPa) were used in this application, the thickness would need to be 0.54 mm. With strong single crystal CVD diamond of the invention (design strength 3.0 MPa), the thickness
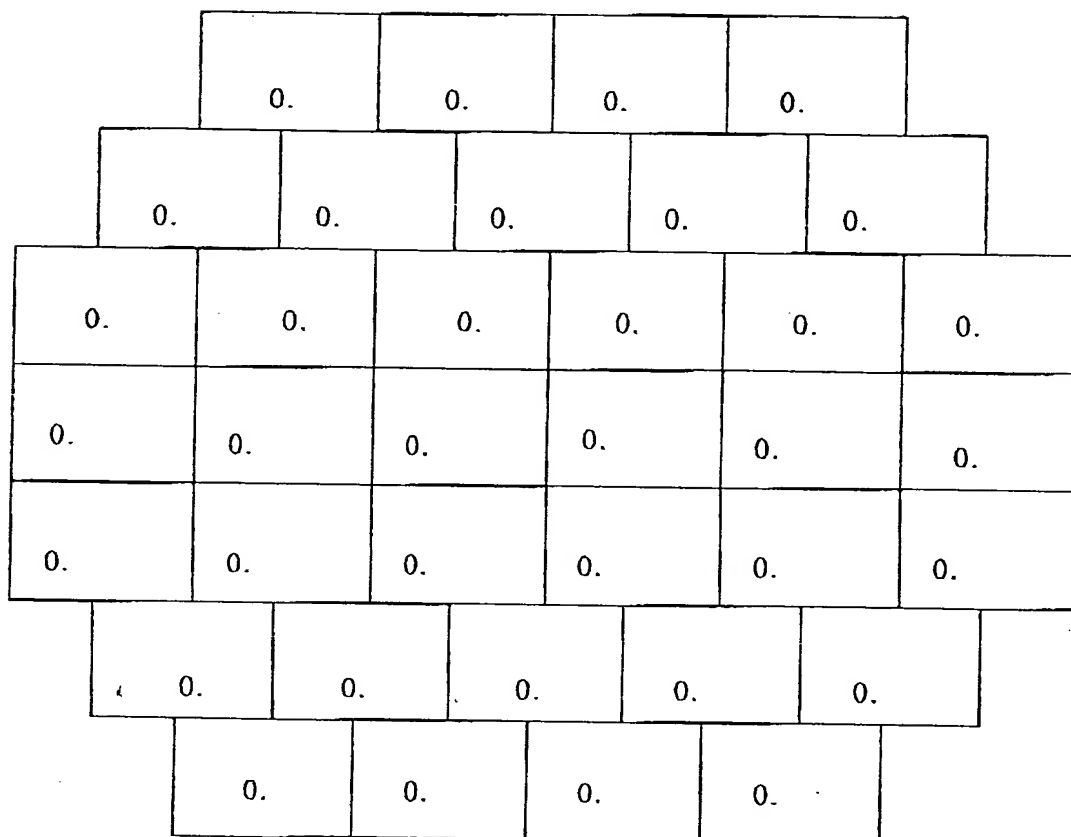
could be reduced to 0.44 mm. The reduction in the thickness of the material will reduce the cost of the window.

Example 3

A set of 3 plates of homoepitaxial CVD diamond were synthesised according to the method described in Example 1. These were prepared as optical plates of thickness 0.60-0.64 mm and with lateral dimensions of up to 6 mm x 6 mm. Sets of Deltascan images, each covering an area of 1 mm x 0.75 mm, were recorded for each sample at a wavelength of 589.6 nm. Each Deltascan sine δ image was analysed for the maximum values of $|\sin \delta|$ and the values of obtained are shown in the $|\sin \delta|$ maps below.

- 38 -

Deltascan map of sample E4.1, showing the maximum value of |sin δ| in each frame of 1 mm x 0.75 mm

Analysis of the data above shows the following

over an area of 2 .0 mm x 2.25 mm the maximum value for |sin δ| is 0.3

over an area of 3 .0 mm x 4.0 mm the maximum value for |sin δ| is 0.6

over an area of 5.25 mm x 4.0 mm the maximum value for |sin δ| is 0.9

Deltascan map of sample E4.2, showing the maximum value of $|\sin \delta|$ in each frame of 1 mm x 0.75 mm

		0.	0.	0.	
0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0..	0.
0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.
	0.	0.	0.	0.	0.

Analysis of the data above shows the following

over an area of 2 .0 mm x 3.75 mm the maximum value for $|\sin \delta|$ is 0.3

over an area of 3 .0 mm x 3.75 mm the maximum value for $|\sin \delta|$ is 0.4

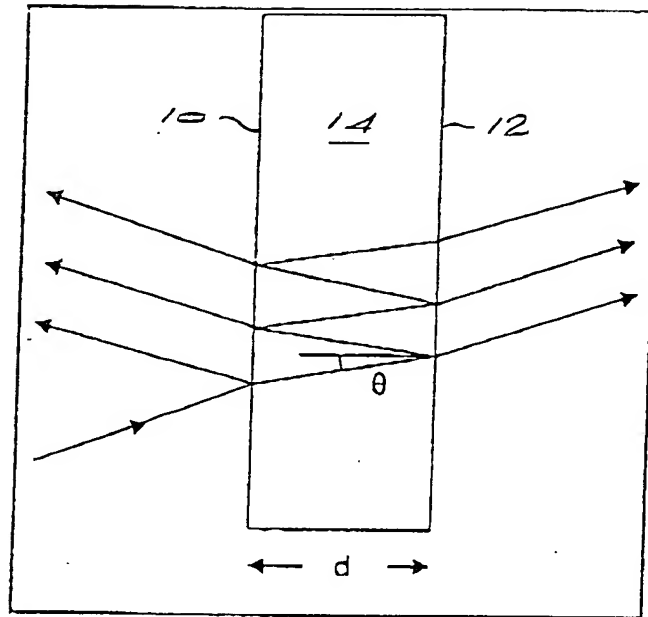over an area of 4.0 mm x 4.5 mm the maximum value for $|\sin \delta|$ is 0.7

Deltascan map of sample E4.3, showing the maximum value of |sin δ| in each frame of 1 mm x 0.75 mm

0.	0.	0.		
0.	0.	0.	0.	0.
0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	

Analysis of the data above shows the following

over an area of 3 .0 mm x 2.25 mm the maximum value for |sin δ| is 0.2

over an area of 3 .75 mm x 3.0 mm the maximum value for |sin δ| is 0.6

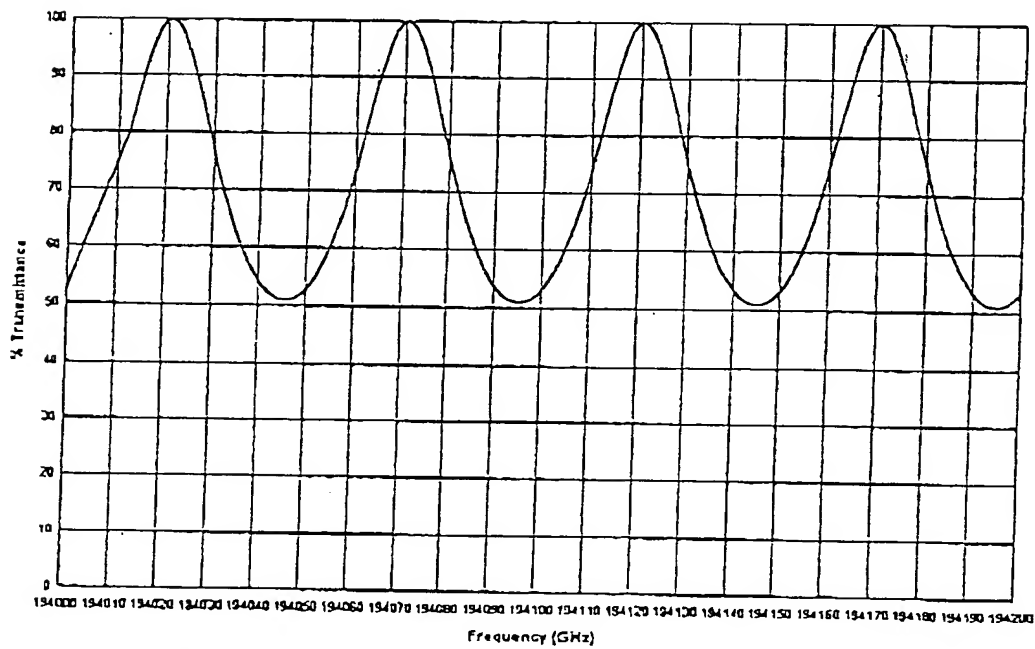over an area of 4.0 mm x 4.5 mm the maximum value for |sin δ| is 0.9

Fig. 1

Fig. 2.

THIS PAGE BLANK (USPTO)